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**Carbonation of alkaline paper mill waste to reduce CO<sub>2</sub> greenhouse gas emissions into the atmosphere**

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## Abstract

The global warming of Earth's near-surface, air and oceans in recent decades is a direct consequence of anthropogenic emission of greenhouse gases into the atmosphere such as CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O and CFCs. The CO<sub>2</sub> emissions contribute approximately 60% to this climate change. This study investigates experimentally the aqueous carbonation mechanisms of an alkaline paper mill waste containing about 55 wt% of portlandite (Ca(OH)<sub>2</sub>) as a possible mineralogical carbon dioxide sequestration process. The overall carbonation reaction includes the following steps: (1) Ca release from the portlandite dissolution, (2) CO<sub>2</sub> dissolution in water and (3) calcium carbonate precipitation. This CO<sub>2</sub> sequestration mechanism was supported by geochemical modelling of final solutions using PHREEQC software, and observations of scanning electron microscope and X-ray diffraction of final reaction products. According to our experimental protocol, the system proposed would favour the total capture of approx. 218 kg of CO<sub>2</sub> into stable calcite per every ton of paper waste, independently of initial CO<sub>2</sub> pressure. The final product from carbonation process is a calcite (ca. 100 wt%)-water dispersion. Indeed, the total captured CO<sub>2</sub> mineralized as calcite could easily be stored in soils or in the ocean without any significant environmental negative impact. This result demonstrates the possibility to use the alkaline liquid-solid waste for CO<sub>2</sub> mitigation and reduction of greenhouse effect gases into the atmosphere.

**Keywords:** *Portlandite; Paper waste; Aqueous carbonation; Mineral trapping of CO<sub>2</sub>; Calcite*

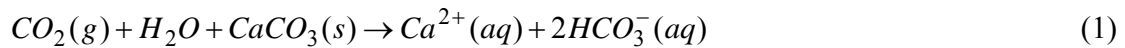
## 1. Introduction

Coal caused the first industrial revolution that transformed the agrarian societies. Electricity allowed the formation of great urban centres. The advance of the industrialized societies has taken place in exchange for the unconditional burning of fossil fuels. This has caused an increase of the CO<sub>2</sub> concentration in the atmosphere from 280 ppm in the pre-industrial revolution to 379 ppm in 2005, rising faster in the last 10 years (average 1995-2005: 1.9 ppm yr<sup>-1</sup>) (IPCC, 2007a).

The temperature of Earth's near-surface, air and oceans is basically controlled by the capacity of the atmosphere to reflect, adsorb and emit the solar energy. However, the continuous emissions of CO<sub>2</sub> into the atmosphere ( $26.4 \pm 1.1$  Gt CO<sub>2</sub> yr<sup>-1</sup> for 2000-2005) have altered this natural equilibrium and have led to the increase of the greenhouse effect and the consequent climatic change. The global surface average temperature will increase 2-4.5 °C when the atmospheric CO<sub>2</sub> concentration doubles the pre-industrial revolution concentration (IPCC, 2007a). These alterations are leading to stress on drinking water availability, species extinction, melting of ice sheets and coastal flooding (IPCC, 2007b).

The energy production system is currently profitable, thus any modification is unviable since it could produce huge imbalances in the global economy. An alternative to reduce the CO<sub>2</sub> emission is the retention of carbon dioxide in natural reservoirs. Three possibilities for sequestration of carbon dioxide are currently being studied: aqueous carbon sequestration, geological carbon sequestration and mineralogical carbon sequestration.

Aqueous carbon sequestration involves the CO<sub>2</sub> dissolution into water to produce a carbonic acid solution, which later is neutralized and equilibrated with limestone as shown by the following reaction (Rau et al., 2007):



63 The dissolved calcium bicarbonate produced is then released and diluted in the ocean where  
64 these ions are already present abundantly in seawater. Moreover, this process is geochemically  
65 comparable to the natural mechanism of CO<sub>2</sub> mitigation by continental and marine carbonate  
66 weathering, but over many millennia time scales (Murray and Wilson, 1997).

67 Geological carbon sequestration consists of capturing gaseous CO<sub>2</sub> from emission sources  
68 and injecting it in terrestrial reservoirs, such as saline aquifers, depleted oil and gas fields or deep  
69 coal seams (Bachu, 2000, 2002; Bachu and Adams, 2003; Friedmann, 2007). The main scientific  
70 concerns involving the geological carbon sequestration applicability are the high pressure and  
71 temperature variations caused by the large CO<sub>2</sub> accumulation on the reservoirs. These  
72 thermodynamic variations could exert forces that diminish the reservoir confinement due to the  
73 formation of cracks and faults either in reservoir itself, or in the cap rocks. Moreover, the CO<sub>2</sub>  
74 dissolution into the pore water and the consecutive carbonic acid formation can result in the rapid  
75 dissolution of several minerals (mainly carbonate, oxides and hydroxide minerals) affecting the  
76 long-term confinement properties of the reservoirs (Kharaka et al., 2006).

77 In terrestrial reservoirs, the CO<sub>2</sub> pressure can decrease in the long term as a consequence of a  
78 mineralogical carbon sequestration or mineral trapping. The stored CO<sub>2</sub> may transform to stable  
79 carbonate minerals by reactions with aqueous ions (mainly calcium, magnesium and iron)  
80 resulting from silicate weathering (Gunter et al., 2000; Kaszuba et al., 2003, 2005; Giammar et  
81 al., 2005; Bénézech et al., 2007). Although this mechanism favours the permanent CO<sub>2</sub>  
82 sequestration, it is expected to be slow in geological formation (hundreds of years) due to the  
83 slow kinetics of silicate mineral dissolution and carbonate mineral precipitation. However, the

mineralogical carbon sequestration could contribute significantly to CO<sub>2</sub> sequestration in the proximity of the emission source, without the need of storing the gas into a geological reservoir. Some authors proposed the use of mineralogical carbon sequestration in controlled reactors as a viable approach to reduce CO<sub>2</sub> emissions into the atmosphere using either: (1) industrial by-products such as coal combustion fly-ash (Montes-Hernandez et al. 2007a), coal combustion fly-ash plus brine solution from gas production (Soong et al., 2006) or municipal solid waste bottom-ash (Rendek et al., 2006); or (2) primary minerals such as serpentine/olivine (Maroto-Valer et al., 2005) or wollastonite (Huijgen et al., 2006). These materials act as calcium and magnesium source favouring the CO<sub>2</sub> retention by carbonate precipitation.

Montes-Hernandez et al. (2007b) proposed an experimental method to synthesize fine particles of calcite by means of aqueous carbonation of pure portlandite at high pressure of CO<sub>2</sub> (initial P<sub>CO2</sub>=55 bar) and moderate and high temperature (30 and 90 °C). This aqueous carbonation process implies dissolution of CO<sub>2</sub> into water and the consequent calcite precipitation. This method also has important ecological implications for mineral carbon sequestration. However, the use of pure portlandite and other primary minerals may suppose a high economic and environmental cost as these are typically resources and not residues.

In the cellulose pulp production for paper manufacture, the dominant process involves cooking woodchips in high concentrations of sodium hydroxide and sodium sulphide for 2-4 h at 170 °C. This process, known as kraft pulping, favours the lignin dissolution and the separation of the cellulose fibers that are recovered by means of sieving. The residual liquids or black liquor containing the most of the dissolved lignin are transformed to white liquor and reused in the cooking stage. This transformation is carried out by both combustion in a boiler and causticizing with lime and implies the production of several types of portlandite-rich solid wastes with alkaline nature known generically as alkaline paper mill wastes.

In some pulp and paper industries, the alkaline by-products are usually sold for the cement manufacture and as alkaline amendment for agricultural soils. Nevertheless, their recycling is limited by the presence of chloride and metals, and in numerous occasions must be stored near the industrial facilities. A few investigations focused on the reusability of these wastes have been reported in the literature, and the existing ones are based on their application for the neutralization of acid mine drainages (Bellaloui et al., 1999). The main aim of this paper is to show the efficiency of the utilization of these wastes as a calcium source for aqueous carbonation, calcite precipitation and mineralogical CO<sub>2</sub> sequestration. From the sustainable development point of view, the treatment proposed is especially attractive because a low-cost residue is used to reduce the emissions of greenhouse gasses into the atmosphere.

## **2. Materials and methods**

### *2.1. Alkaline paper mill waste*

The alkaline paper waste used in the present study was collected from a cellulose pulp factory (ENCE) located in Huelva, south-western Spain. This by-product, so-called calcium mud, is the waste of the calcination or conversion of calcium carbonate to lime for the causticizing of the black liquor. Calcium mud was selected since it presents a higher Ca content than the remaining alkaline paper wastes.

The particle size of paper mill waste ranges from 1 to 100 µm with a median size of 15 µm, as determined by laser diffraction. This waste is made up of portlandite (Ca(OH)<sub>2</sub>; 55 wt%), calcite (CaCO<sub>3</sub>; 33 wt%) and hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>; 12 wt%). The portlandite

particles present a laminar-pseudohexagonal habit, as observed by scanning electron microscopy equipped with an energy dispersive system (SEM-EDS, JEOL JSM-5410 instrument) (Fig. 1). The chemical composition analyzed with X-ray fluorescence (XRF, BRUKER PIONEER instrument) shows high content of Ca (83.2 wt% CaO), C (10.3 wt% CO<sub>2</sub>), P (2.4 wt% P<sub>2</sub>O<sub>5</sub>), S (2 wt% SO<sub>3</sub>), Na (0.88 wt% Na<sub>2</sub>O), Mg (0.35 wt% MgO), Si (0.34 wt% SiO<sub>2</sub>), Al (0.17 wt% Al<sub>2</sub>O<sub>3</sub>) and K (0.13 wt% K<sub>2</sub>O), and minor amounts of Cl (590 ppm), Fe (137 ppm), Ni (130 ppm), Sr (114 ppm) and Cu (108 ppm). The water content determined by drying at 105 °C until constant weight was about 21 wt%. The presence of high concentrations of portlandite in paper mill waste accounts for the high alkalinity and potential for carbon dioxide sequestration as discussed below.

## 2.2. CO<sub>2</sub> sequestration experiments

The CO<sub>2</sub> sequestration experiments were conducted in a 2 L (total volume) closed titanium-lined pressure reactor (Parr Instrument Co., USA, Model 4843) equipped with a heating jacket (Fig. 2). In each experiment, the autoclave was charged with approximately 1L of Millipore MQ water (18.2 MΩ) and 20 g of paper mill waste. The waste particles were immediately dispersed with mechanical agitation (450 rpm) and the dispersion heated to 30 or 60 °C. When the temperature was reached, 10, 20, 30 or 40 bar of CO<sub>2</sub> (provided by Linde Gas S.A.) was injected into the reactor by opening a valve and adjusting the pressure to the desired one, and the reaction was commenced. This initial pressure of CO<sub>2</sub> was equal to the total initial pressure in the system. A summary of the experiments carried out and the initial experimental conditions is shown in Table 1. A long-term experiment (48 hours) at 30 bar of initial pressure of CO<sub>2</sub> allowed us to



both optimize the experimental duration of the remaining experiments at 2 hours and study the kinetic evolution of the carbonation process.

The global pressure drop in the system,  $P_{global\_pressure-drop}$ , is a consequence of both the dissolution-dissociation of  $CO_2$  in the solution and aqueous carbonation process of  $Ca(OH)_2$ . In order to calculate the pressure drop only produced by the carbonation process ( $P_{carbonation\_pressure-drop}$ ), two independent but complementary experiments were proposed for each experiment: (1) to measure the pressure drop related to the dissolution-dissociation of  $CO_2$  into pure water ( $P_{water\_pressure-drop}$ ), and (2) to measure the pressure drop related to the dissolution-dissociation of  $CO_2$  in a Ca-rich solution ( $P_{Ca-rich\_pressure-drop}$ ). In this second experiment, a concentration of  $1\text{ g L}^{-1}$  of calcium was chosen, that represented the average concentration after paper waste dispersion in water. These two experiments demonstrated that the Ca-concentration ( $0\text{-}1\text{ g L}^{-1}$ ) has no measurable effect on the dissolution-dissociation of  $CO_2$  since the monitored pressure drop in pure water ( $P_{water\_pressure-drop}$ ) was equivalent to the monitored pressure drop in presence of Ca ( $P_{Ca-rich\_pressure-drop}$ ). Consequently, the pressure drop produced by the carbonation process of  $Ca(OH)_2$  was calculated by a simple pressure balance:

$$P_{carbonation\_pressure-drop} = P_{global\_pressure-drop} - P_{water\_pressure-drop} \quad (2)$$

Under isothermal conditions,  $P_{global\_pressure-drop}$  and  $P_{water\_pressure-drop}$  are proportional to the initial  $CO_2$  pressure.

At the end of the experiment, the reactor was removed from the heating system and was immersed in cold water. The reaction cell was depressurized during the cooling water period at

25 °C (about 15 minutes). Subsequently, the reactor was disassembled and the supernatant was separated from the solid product by centrifugation at 12,000 rpm for 30 minutes. Finally, the solid product was dried directly in the centrifugation flasks for 48 h at 65 °C. The supernatant solutions were filtered through a 0.2-µm Teflon filter. Adsorption on the filter and filter holder was considered negligible. The filtered solutions were immediately acidified for measurement of [Ca], [Ni], [Zn], [Cu] and [Sr] by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES).

### *2.3. Characterization of solid phase*

The mineralogical characterization of the starting material and solid products was carried out by X-ray diffraction (XRD, powder method) using a D501 SIEMENS diffractometer. Working conditions were CoK $\alpha$  monochromatic radiation ( $\lambda=1.7902 \text{ \AA}$ ), 37.5 mA and 40 kV. The experimental measurement parameters were 12 s counting time per 0.02° 2 $\theta$  step in the 5-80° 2 $\theta$  range. The detection is performed by a Kevex Si(Li) detector. Morphological analyses of solid products were also characterized by means of SEM-EDS.

Solution saturation indexes with respect to solid phases ( $SI=\log(IAP/K_S)$ , where SI is the saturation index, IAP is the ion activity product and  $K_S$  is the solid solubility product) and aqueous speciation of the leachates were calculated using the equilibrium geochemical speciation/mass transfer model PHREEQC (Parkhurst and Appelo, 2005) and the database of the speciation model MINTEQ. Zero, negative or positive SI values indicate that the solutions are saturated, undersaturated and supersaturated, respectively, with respect to a solid phase.

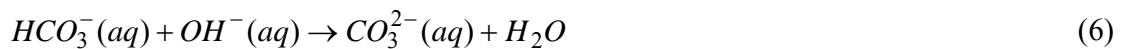
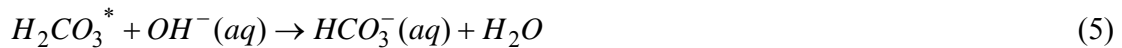
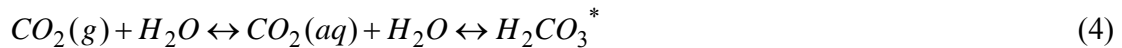
### 3. Results and discussion

#### 3.1. Reaction mechanisms of CO<sub>2</sub> sequestration

In an aqueous system, the water-CO<sub>2</sub>-paper waste interaction would suppose the carbonation of portlandite (Ca(OH)<sub>2</sub>; 55 wt%) according to well-known reactions (3-7) described in numerous works (e.g., Juvekar and Sharma, 1973; Shih et al., 1999; Beruto and Botter, 2000). On one hand, the calcium hydroxide is dissociated and increases the pH up to values around 12 (Eq. 3):



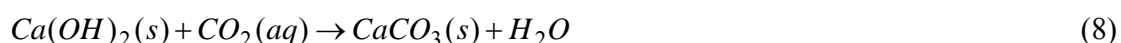
On the other hand, the gaseous CO<sub>2</sub> is dissolved into the solution and reacts with the water to form carbonic acid (Eq. 4). Once equilibrium is established between the gaseous CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub>, the carbonic acid further dissociates into bicarbonate and carbonate ions (Eqs. 5 and 6). At alkaline pH, the carbonate ion (CO<sub>3</sub><sup>2-</sup>) is the dominant species occurring in solution.



The presence of CO<sub>3</sub><sup>2-</sup> anions together with high Ca concentrations from the portlandite dissolution favours the supersaturation, and hence, the precipitation of calcium carbonate (Eq. 7):



The overall reaction for the process can be written as:



The thermodynamic calculations and the mineralogical characterization of solid products after experiments suggest that this simple reaction mechanism explains the CO<sub>2</sub> sequestration by paper mill waste. After the reaction, PHREEQC code indicates that the solutions are supersaturated with respect to calcium carbonate. Saturation indexes of calcite are in the range 1.13-1.71 (Table 1). Comparison of X-ray diffraction spectra of the starting material and the solid product demonstrates that the portlandite contained in the starting material is totally carbonated and transformed to calcite (Fig. 3). The precipitated calcite is characterized by micrometric agglomerates of rhombohedral-crystals (Fig. 4). Both pre-existing calcite and hydroxyapatite in the starting material do not intervene in the CO<sub>2</sub> sequestration process.

One possible disadvantage of using paper mill waste is that this waste contains initially some toxic elements such as Ni, Zn, Cu and Sr that may be released in solution. However, the carbonation process also favoured the co-precipitation and/or incorporation of the dissolved impurities into the calcite crystal lattice. In fact, the Ni, Zn and Cu concentrations were below detection limit (< 6 µg L<sup>-1</sup>). Strontium was the only trace element detected by ICP-AES ([Sr] ≈ 0.25 mg L<sup>-1</sup>) in the solution. Nevertheless, the Sr concentrations are lower than the ones that

should have a pre-potable water for human consumption according to the established requirements by World Health Organisation (4 mg L<sup>-1</sup>).

In summary, the final product from carbonation process is a solid containing ca. 100 wt% of calcite, as occurs with the experiments from Montes-Hernandez et al. (2007b), but using a low-cost portlandite-rich waste instead of pure portlandite. Moreover, taking into account that the paper mill waste does not favour the liberation of toxic metallic ions at the CO<sub>2</sub> sequestration experiments, the final calcite-water dispersion could be used as reagent for a further aqueous carbon sequestration (see Introduction, Eq. 1). Hence, the final result of these experiments would allow us to continue sequestering CO<sub>2</sub> and the total amount of captured CO<sub>2</sub> could be poured either directly into the sea (not contribute with trace elements), being even beneficial for marine biota (Rau et al., 2007) or into soils.

### 3.2. Amount of sequestered CO<sub>2</sub>

A simplified method was developed to estimate the quantity of CO<sub>2</sub> sequestered by carbonate precipitation. This method was partially described in the section 2.2. Herein, the pressure drop produced by the carbonation process of Ca(OH)<sub>2</sub> (Eq. 8) in the system was calculated by a simple pressure balance (Eq. 2). Knowing the pressure drop values in each experiment (Table 1), the amount of CO<sub>2</sub> consumed by calcite precipitation ( $n_{carbonation\_CO_2,real}$  in mol) could be calculated using the ideal gas law:

$$n_{carbonation\_CO_2,real} = \frac{P_{carbonation\_pressure-drop} V}{RT} \quad (9)$$

where  $V$  is the reactor volume occupied with gas (1 L),  $T$  is the reaction temperature ( $\approx 303$  °K) and  $R$  is the gas constant ( $0.08314472$  L bar K<sup>-1</sup> mol<sup>-1</sup>).

In experiments at 30 °C and 2 h of experimental duration, the pressure drop by portlandite carbonation was around 2.5 bar, independently of initial CO<sub>2</sub> pressure (Fig. 5a). Although the results of the long-term experiment (48 h, 30 bar and 30 °C) show that the equilibrium is obtained after about 5 hours of solid-fluid interaction, the maximum pressure drop by carbonation is already reached at 2 hours of experiment (Fig. 5b), and thus the experimental duration of the remaining experiments was correctly optimized. According to Eq. 9, the real amount consumed by carbonation was of 0.09923 mol of CO<sub>2</sub>.

The theoretical amount of CO<sub>2</sub> ( $n_{carbonation\_CO_2,theoretical}$ ) that should be sequestered by carbonation process (i.e., if all calcium is carbonated) could be calculated based on both the stoichiometry of reaction (8) and the quantity of portlandite contained into the paper mill waste (55 wt%):

$$n_{carbonation\_CO_2,theoretical} = \frac{w_{Ca(OH)_2}}{M_{Ca(OH)_2}} \quad (10)$$

where  $M_{Ca(OH)_2}$  is the molar mass of Ca(OH)<sub>2</sub> (74.093 g mol<sup>-1</sup>) and  $w_{Ca(OH)_2}$  is the starting mass of Ca(OH)<sub>2</sub> in the reactor (8.69 g) which was calculated as follows:

$$w_{Ca(OH)_2} = m_{paper\_waste} \times \left( \frac{\%portlandite}{100} \right) \times \left( 1 - \frac{\%water\_content}{100} \right) \quad (11)$$

where  $m_{paper\_waste}$  is the mass of paper mill waste used in the experiments (20 g),  $\%_{portlandite}$  is the percentage of portlandite in the waste (55 wt%) and  $\%_{water\_content}$  is the water content percentage in the waste (21 wt%). The theoretical amount of CO<sub>2</sub> that should be sequestered is 0.11729 mol. This supposes a carbonation efficiency ( $CE$ ) of 85% at 30 °C according to:

$$CE = \frac{n_{carbonation\_CO_2,real}}{n_{carbonation\_CO_2,theoretical}} \times 100 \quad (12)$$

In the experiment at high temperature (60 °C, 30 bar), the pressure drop by carbonation is slightly superior (3 bar), albeit the sequestered amount of CO<sub>2</sub> and the carbonation efficiency are very similar since this process depends inversely on the reaction temperature (Eq. 9).

Theoretically, the extrapolation of this experiment to real industrial scale would suppose a maximum CO<sub>2</sub> sequestration capacity of 258.54 kg of CO<sub>2</sub> per every ton of paper mill waste containing 55 wt% of portlandite. However, with our experimental protocol, 218.37 kg of CO<sub>2</sub> per every ton of paper mill waste could be successfully sequestered into stable calcite. Obviously, this is an attractive result concerning the mineral trapping of CO<sub>2</sub>.

### 3.3. Kinetic modelling of sequestered CO<sub>2</sub>

The monitoring of the pressure drop for any controlled system under ideal gas conditions allows the kinetic modelling of sequestered CO<sub>2</sub> after gas injection in a solid-liquid system (paper mill waste-water dispersion for this study). This can be done using a simple correlation function,

$n_{total\_CO_2} = f(t)$ , where  $n_{total\_CO_2}$  is the total mol quantity of sequestered  $CO_2$  in the paper waste-water dispersion and  $t$  is the time after gas injection.

Several kinetic models including first-order, pseudo-first-order, second-order, pseudo-second-order, parabolic diffusion and power function kinetic expressions are reported in the literature for fitting the kinetic experimental or calculated data of solid-fluid interaction processes (e.g. Lagergren, 1898; Ho and Mckay, 1999). For this study, the kinetic modelling concerns the total sequestered quantity of  $CO_2$  in a paper mill waste-water dispersion, i.e. the  $CO_2$  dissolution-dissociation in water, possibly the  $CO_2$  adsorption on the paper waste and, sequestered  $CO_2$  by carbonation process. For this case, the best fit (attested by a correlation factor close to 1) of the experimental-calculated data was achieved when using a pseudo-second-order kinetic model according to the following expression:

$$\frac{dn_{total\_CO_2,t}}{dt} = k_s (n_{total\_CO_2,max} - n_{total\_CO_2,t})^2 \quad (13)$$

where  $k_s$  is the rate constant of sequestered  $CO_2$  [ $mol^{-1} s^{-1}$ ] for a given initial pressure of  $CO_2$  in the system,  $n_{total\_CO_2,max}$  is the maximum sequestered quantity of carbon dioxide at equilibrium [mol],  $n_{total\_CO_2,t}$  is the sequestered quantity of carbon dioxide at any time,  $t$ , [mol].

The integrated form of Eq. 13 for the boundary conditions  $t = 0$  to  $t = t$  and  $n_{total\_CO_2,t} = 0$  to  $n_{total\_CO_2,t} = n_{total\_CO_2,t}$  is represented by a hyperbolic equation (Eq. 14):



$$n_{total\_CO_2,t} = \frac{n_{total\_CO_2,max} \times t}{\left( \frac{1}{k_s \times n_{total\_CO_2,max}} \right) + t} \quad (14)$$

In order to simplify the fitting of experimental-calculated data, we have defined the constant  $t_{1/2} = 1/k_s \times n_{total\_CO_2,max}$ . Physically,  $t_{1/2}$  represents the time after which half of the maximum sequestered quantity of carbon dioxide was reached and is called “half-sequestered CO<sub>2</sub> time”. It can be used to calculate the initial rate of sequestered CO<sub>2</sub>,  $v_{0,s}$ , [mol s<sup>-1</sup>] (Eq. 15):

$$v_{0,s} = \frac{n_{total\_CO_2,max}}{t_{1/2}} = k_s (n_{total\_CO_2,max})^2 \quad (15)$$

The fitting of the experimental-calculated kinetic curve at 30 bar and 30 °C ( $n_{total\_CO_2,t}$  vs.  $t$ ) using Eq. 14 is shown in Figure 6. The parameters  $t_{1/2}$  and  $n_{total\_CO_2,max}$  were estimated by applying non-linear regression using the least squares method. The initial rate of sequestered CO<sub>2</sub> was calculated using the Eq. 15 ( $v_{0,s} = 3.3 \times 10^{-4}$  mol s<sup>-1</sup>) at 30 °C. This value indicates that the mass transfer of compressed CO<sub>2</sub> in contact with solid-water dispersion is higher than CO<sub>2</sub> transfer at atmospheric conditions or at low pressure (Akanksha et al., 2007; Haubrock et al., 2007).

#### 4. Remarks and conclusions

In search of the most effective technique to reduce the point CO<sub>2</sub> emissions into the atmosphere, the aqueous carbonation of alkaline paper mill waste (approx. 55 wt% in portlandite) could fulfil all necessary expectations for the following reasons:

1. The CO<sub>2</sub> sequestration is mainly produced by the portlandite dissociation, CO<sub>2</sub> dissolution and calcite precipitation, as shown by means of XRD and SEM-EDS techniques, and thermodynamic calculations with PHREEQC. According to our estimations, the system proposed in this study would favour the mineralogical sequestration of approx. 218.37 kg of CO<sub>2</sub> into stable calcite per every ton of paper waste. The amount sequestered by carbonation is independent of both temperature (30 or 60 °C) and initial pressure of CO<sub>2</sub> injected in the system (10, 20. 30 or 40 bar).
2. The independence of temperature and pressure in the sequestration efficiency, probably owing to that the reaction between portlandite and CO<sub>2</sub> is extremely fast, could reduce the costs for the process in a industrial scale since: (1) additional energy is not required for the excessive increasing of both parameters and (2) the system does not need special materials for reactors design.
3. The capacity of mineral CO<sub>2</sub> sequestration of alkaline paper mill waste is much higher than those in other materials reported in the literature. As a comparison, the municipal solid waste bottom-ash could sequester 23.08 kg of CO<sub>2</sub> per ton (Rendek et al., 2006) and coal combustion fly-ash 26.19 kg of CO<sub>2</sub> per ton (Montes-Hernandez et al. 2007a), that is, both wastes present a sequestration capacity ca. 10 times lower than paper wastes. Wollastonite presents a sequestration capacity very similar, i.e. 329 kg of CO<sub>2</sub> per ton (Huijgen et al., 2006); however, this primary mineral is not a residue.

4. The result from carbonation process is a free-metal solution in contact with a solid containing practically 100 wt% of calcite. This final product could be used as reagent for a further aqueous carbon sequestration. The result of this additional CO<sub>2</sub> sequestration may be stored in the ocean where it would add minimally to the large, benign pool of these ions already present in seawater.
5. The generation of a solid product containing ca. 100% calcite also revalues the original waste since this mineral is amply used in rubber, plastic, printing ink, paper making dope, oil point, toothpaste, cosmetics and food industries (Chan et al., 2002; Kugge and Daicic et al., 2004).
6. The utilization of other wastes to sequester CO<sub>2</sub> would result in the production of calcite in a matrix of silicate minerals that would continue constituting a waste with low application. In addition, these final products could be neither used for a further aqueous carbon sequestration nor stored in soils or in the ocean.
7. The carbonation is an exothermic process for portlandite (Montes-Hernandez et al., 2007b), which potentially reduces the overall energy consumption and costs of carbon sequestration.

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396

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## Tables

Table 1. Experimental conditions and results of CO<sub>2</sub> sequestration experiments using paper mill waste. Saturation state of calcite was calculated simulating with PHREEQC the reaction between Millipore MQ water (pH 5.6) and portlandite (8.69 g) for different initial conditions of temperature and CO<sub>2</sub> pressure.

## Figure captions

Figure 1. SEM image of paper mill waste before experimentation showing the initial crystals of portlandite, calcite and hydroxyapatite.

Figure 2. Schematic experimental system for sequestration of CO<sub>2</sub> by aqueous carbonation of paper mill waste in a continuously stirred reactor.

Figure 3. XRD patterns of starting paper mill waste and solid products after carbonation during 2 and 48 h. C: Calcite, P: Portlandite, H: Hydroxyapatite. These spectra demonstrate the total consumption of portlandite and the production of calcite.

Figure 4. (a-b) SEM images of calcite particles precipitated during CO<sub>2</sub> sequestration experiments.

500 Figure 5. (a) Linear correlation between the pressure drop and the initial pressure of CO<sub>2</sub> for  
501 experiments at 30 °C, an initial pressure of CO<sub>2</sub> equal to 10, 20, 30 and 40 bar and 2 h of  
502 carbonation. (b) Kinetic behaviour of the CO<sub>2</sub> pressure drop in the long-term experiment (48 h) at  
503 30 °C and 30 bar of initial pressure of CO<sub>2</sub>. In both, constant pressure drop of 2.5 bar is  
504 independent on the initial pressure of CO<sub>2</sub>, showing that the thermodynamic state of CO<sub>2</sub>  
505 (gaseous or supercritical) does not modify the kinetics of reaction.

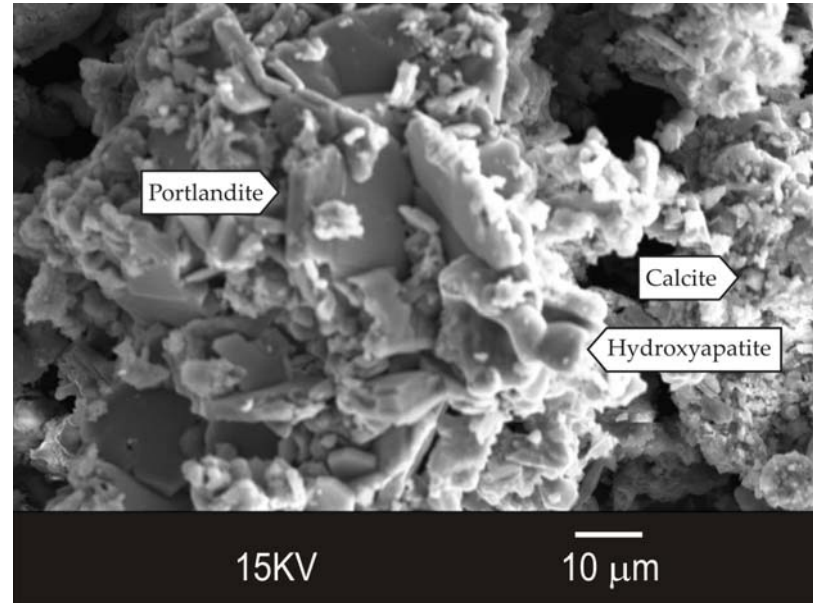
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507 Figure 6. Kinetic modelling of sequestered quantity of CO<sub>2</sub> in the long-term experiment (48 h) at  
508 30 °C and 30 bar of initial pressure of CO<sub>2</sub>.

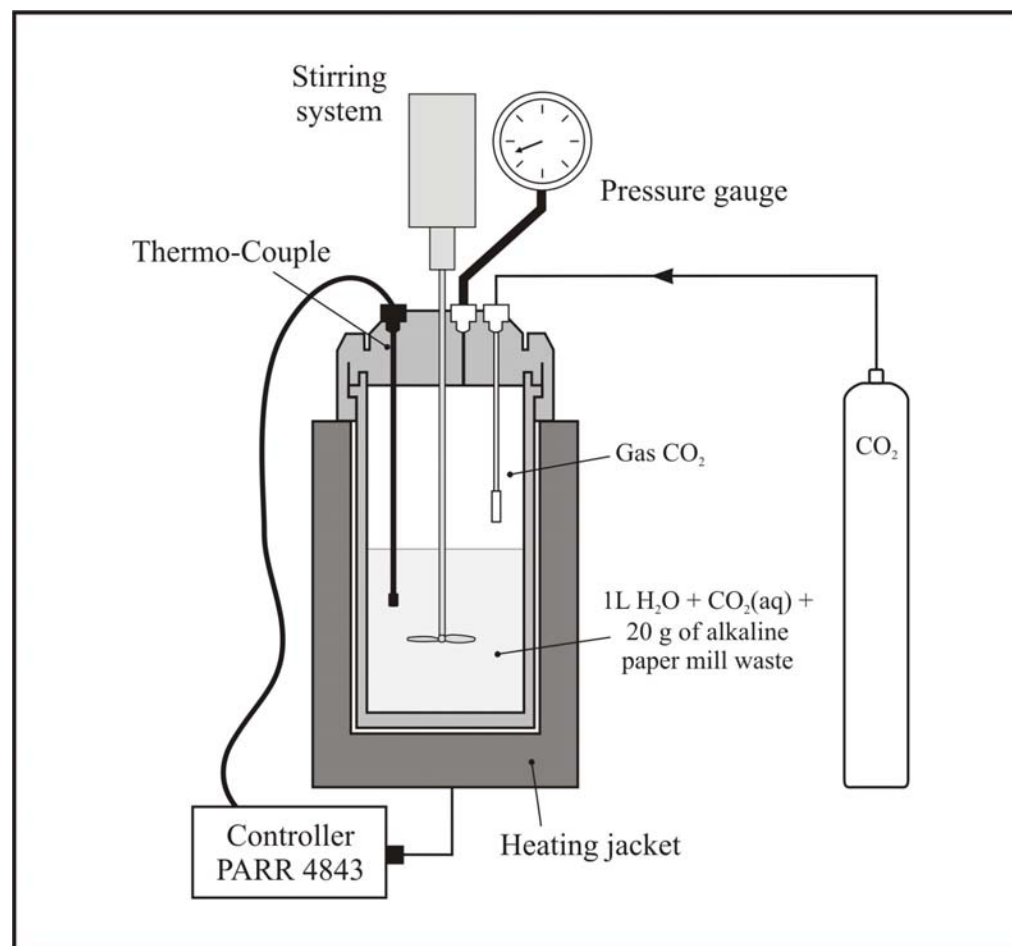
Experiment	Reactor content	Duration (h)	Temp. (°C)	Initial CO <sub>2</sub> pressure (bar)	Final CO <sub>2</sub> pressure (bar)	CO <sub>2</sub> pressure-drop (bar)	Carbonation pressure (bar)	SI <sub>calcite</sub>
Experiment 1	Blanks*	2	30	40	30.5	9.5	-	-
	1L pure water + 20 g of paper waste	2	30	40	28	12	2.5	1.13
Experiment 2	Blanks*	2	30	30	22.5	7.5	-	-
	1L pure water + 20 g of paper waste	2	30	30	20	10	2.5	1.25
Experiment 3	Blanks*	2	30	20	15	5	-	-
	1L pure water + 20 g of paper waste	2	30	20	12.5	7.5	2.5	1.42
Experiment 4	Blanks*	2	30	10	7.5	2.5	-	-
	1L pure water + 20 g of paper waste	2	30	10	5.3	4.7	2.2	1.71
Experiment 5	Blanks*	48	30	30	21.5	8.5	-	-
	1L pure water + 20 g of paper waste	48	30	30	19	11	2.5	1.25
Experiment 6	Blanks*	2	60	30	24.5	5.5	-	-
	1L pure water + 20 g of paper waste	2	60	30	21.5	8.5	3	1.52

\*Blanks include two experiments of dissolution-dissociation of CO<sub>2</sub>: (1) into pure water and (2) into a solution containing 1 g L<sup>-1</sup> of Ca. Both experiments showed identical results.

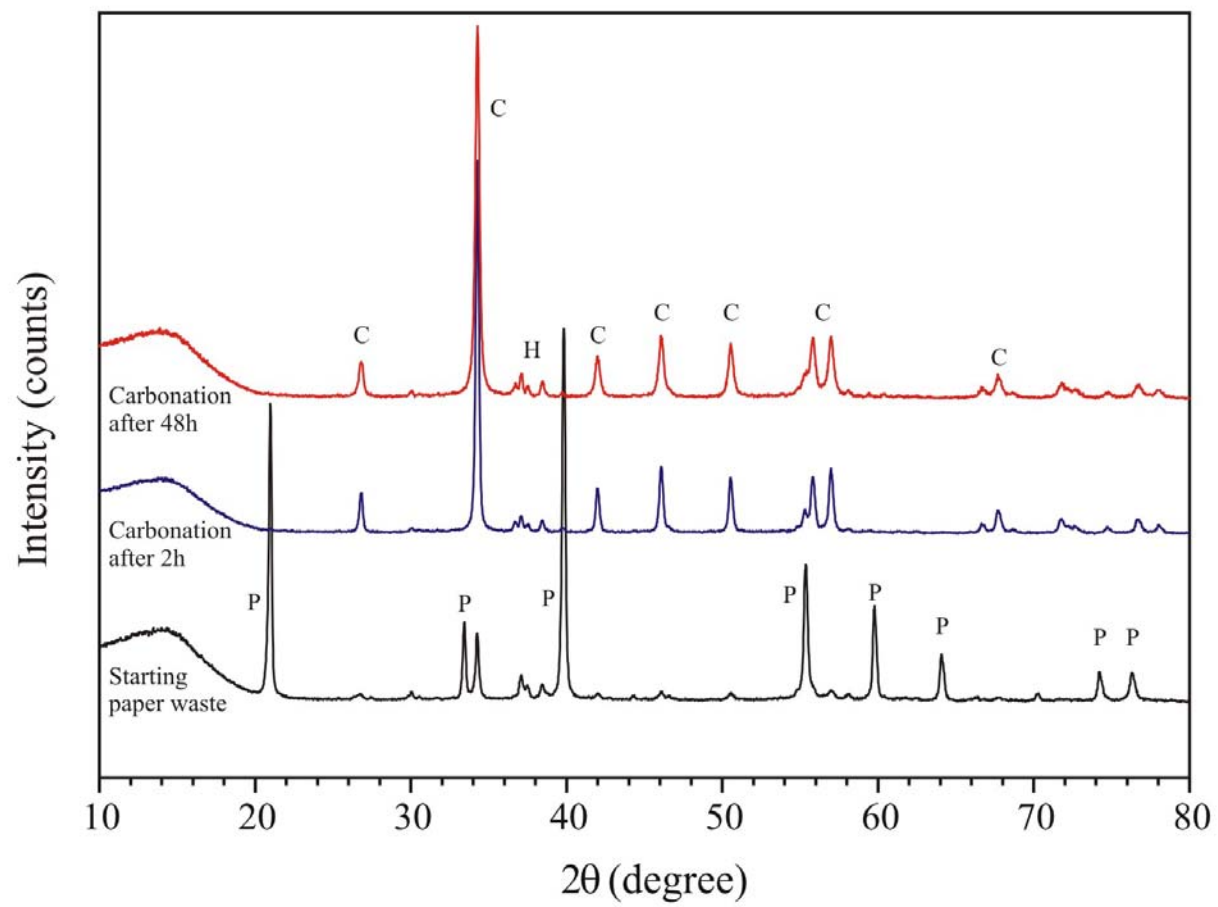
**Table 1**



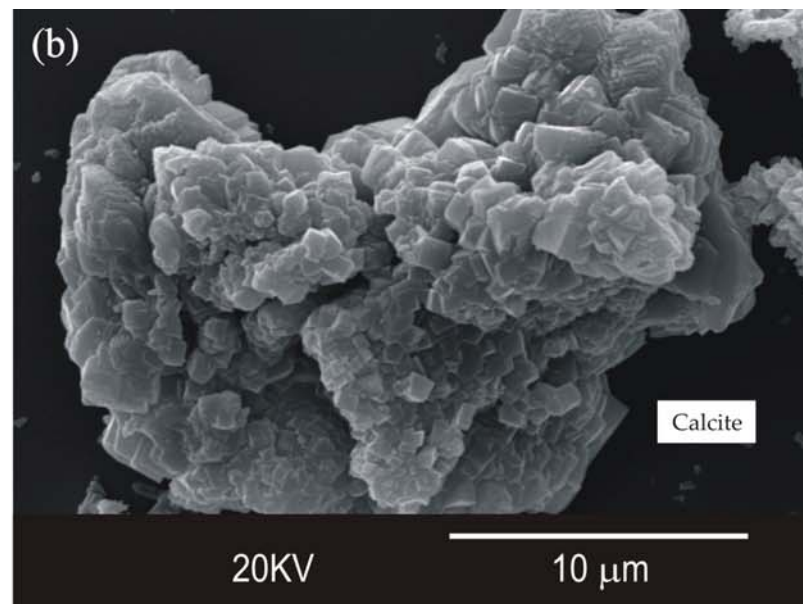
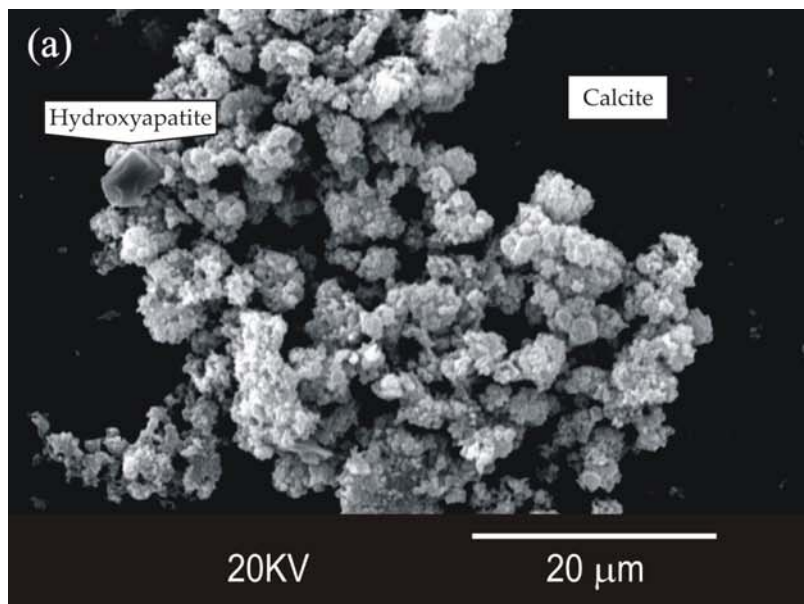
**Figure 1**



**Figure 2**



**Figure 3**



**Figure 4**

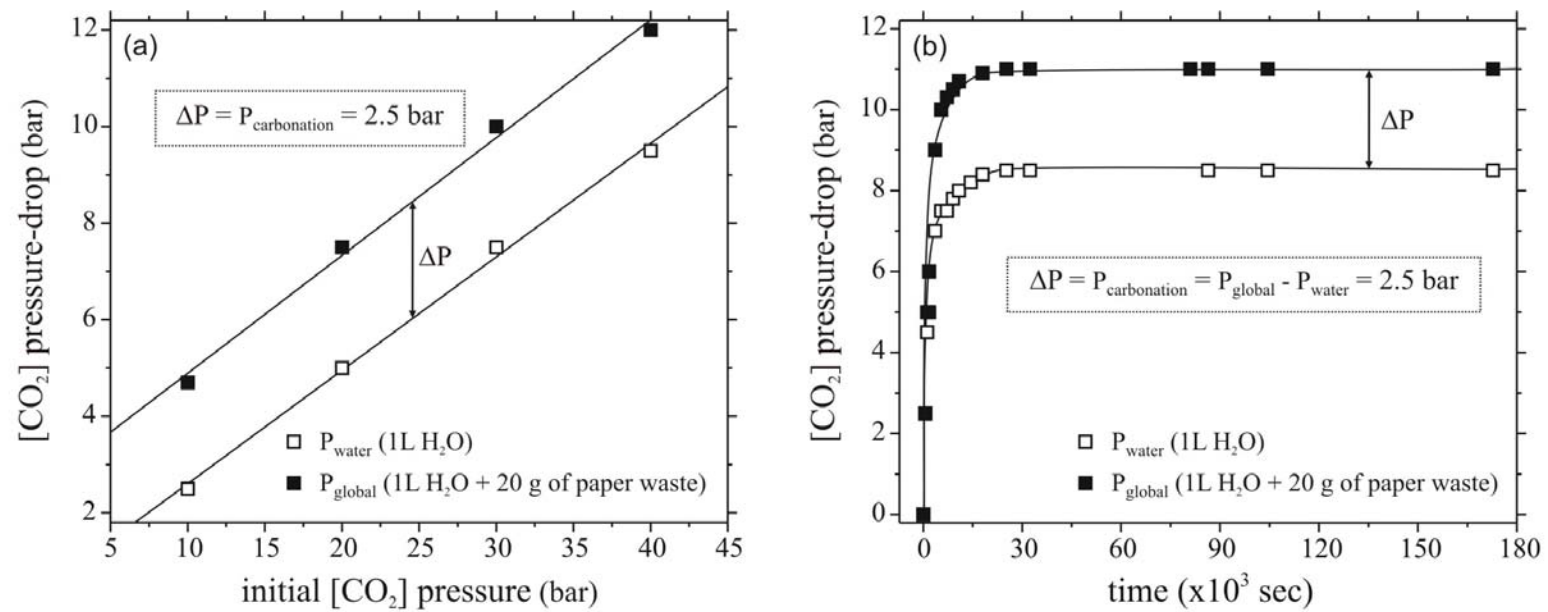
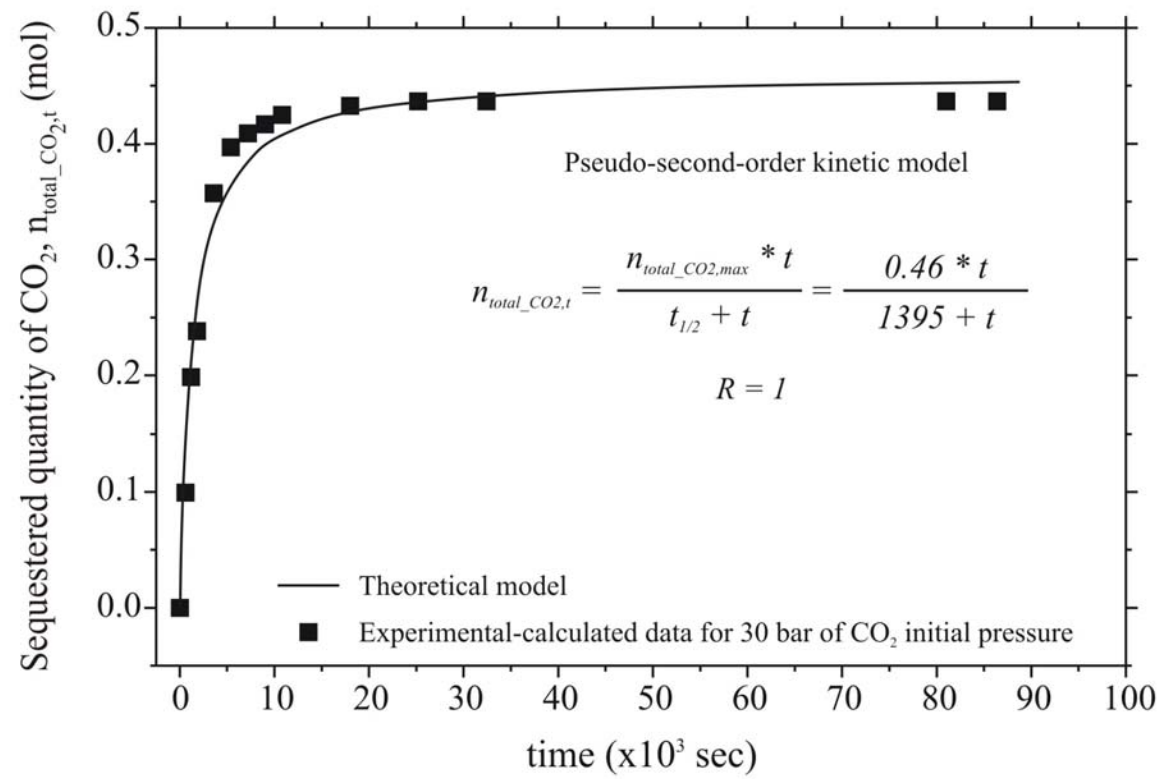


Figure 5





**Figure 6**